IMPROVED X-RAY DIFFRACTION TECHNIQUES APPLIED TO THE DEVELOPMENT OF NEW TYPES OF METAL ELECTRODEPOSITS

BY

STANLEY HAROLD SIMONSEN

A.B., Iowa State Teachers College, 1940
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

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Introduction

One of the major developments, due to the costliness of both nickel and nickel buffing, in the electrodeposition of nickel was the introduction of commercially successful bright nickel plating by Schlötter (1) in 1934. Two widely accepted theories have been proposed for the explanation of the luster of bright electrodeposits: (a) a high degree of preferred orientation so that the crystal faces presented to the surface are essentially parallel results in a bright deposit, or (b) if the grain size of the deposit is smaller than the wave length of visible light, the deposit will be bright.

The purpose of this investigation was to make a critical and extensive new study of matte, semi-bright and bright electrodeposited nickel by refined instrumental techniques not available to most earlier workers. A large number of specimens deposited under varied conditions were examined by improved x-ray diffraction techniques in an attempt to attain a statistical view of the structure of nickel deposits as it is related to many independent and dependent variables such as chemical nature of the bath, pH, current density, thickness, organic additions, etc. Physical properties such as orientation, grain size, and stress were evaluated in order to determine if any correlation existed between these measurable characteristics and the fundamental optical property of brightness.

Experimental

All of the electrodeposits were examined by transmission of the x-ray beam through the edges of the specimens at an angle of 45° to the fiber axis, which is always normal to the

surface of the cathode. Diffraction patterns were also made from the surface of the specimens with the North American Philips Geiger-Counter X-Ray Spectrometer in order to obtain the intensities of the diffraction rings.

The indices of the fiber axes were determined by comparing the x-ray patterns with theoretical patterns calculated by assuming various crystallographic directions parallel to the fibering direction (2).

Test panels of matte, semi-bright and bright nickel were deposited from baths of various compositions and under various conditions of current density, metallic impurities, and organic breakdown products of addition agents. One series was plated in a Hull cell so that the current density could be varied continuously and all other variables kept constant.

Formvar replicas of the as-plated surfaces of matte and semi-bright nickel deposits were made by the technique of Schaefer and Harker (3) and electron micrographs were made of the replicas.

The stress present in the electrodeposited nickel was determined by measuring the convexity of spring steel strips before and after electrodeposition and applying the formula of Phillips (4). Microscopic cracks if present in the deposits invalidated the stress measurements.

Conclusions and Summary

1. The orientation of the nickel electrodeposits varied with bath conditions such as composition, current density, impurities and addition agents and with thickness. The [100], [110], [100] + [110], [120], [112] and [120] + [110] fiber axes were observed as well as a random distribution. The predominate orientation found was the [100] fiber axis.

2. The anomalous meridial intensity maximum present on the (200) ring of the deposits having a [100] fiber axis was found to be due to twinning on the (111) plane.

3. Geiger spectrometer patterns were useful in evaluating abnormal intensities, but they were not adequate for uniquely determining the fiber axes.

4. The x-ray grain sizes of the matte, semi-bright and bright nickel deposits were very similar and thus the difference in luster could not be mainly due to difference in grain size. Semi-bright deposits were observed in which both matte and semi-bright areas were present on the same panel. These different areas showed the same x-ray grain size.

5. It was found from the large number of electrodeposited nickel panels examined that no correlation existed between the orientation of the nickel crystals and the brightness of the deposit. The matte deposits often had as high a degree of preferred orientation as the bright deposits, and many of the deposits with the brightest luster had a random distribution of crystals.

6. A definite correlation existed between the stress present in the electrodeposited nickel and the orientation of the deposits. In deposits from Watts and Perflow baths containing no impurities four stress areas or bands were observed: (1) the [100] orientation produced the lowest stress, (2) a narrow band of higher stress with random distribution, (3) a band of still higher stress with [110] orientation, and (4) the highest stress produced by random distribution.

It is interesting to note that the deposits in the highest stress band were very brittle and adhered poorly to the base metal.

7. Large concentrations of the organic breakdown products of the Perflow addition agent caused the orientation of the electrodeposited nickel to change from [100] to random distribution.

8. Deposits of commercial thickness from the same type bath and plated under identical conditions showed the same orientation on steel, cold rolled brass or annealed brass.

9. The electron micrographs of as-plated surfaces of matte and semi-bright nickel deposits showed that there is a correlation between brightness of a nickel electrodeposit and submicroscopic smoothness of the deposit.

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VITA

The author was born August 25, 1918, at Missoula, Montana. He attended the public schools through the second year of high school in Sewickley, Pennsylvania, and was graduated from Coraopolis, Pennsylvania, Senior High School in June, 1935.

After working one year at the Standard Steel Spring Company, Coraopolis, the author entered Iowa State Teachers College in September, 1936, and received the degree of Bachelor of Arts in August, 1940. He served the Winter Quarter, 1940, as full time assistant in the Chemistry Department. From November, 1940, to July, 1944, he was employed as an analytical chemist by the Vanadium Corporation of America, Bridgeville, Pennsylvania. He also taught a Pennsylvania State College Extension course in Analytical Chemistry at night for two years during this period.

In July, 1944, the author entered military service as a private in the Army of the United States and served as medical laboratory technician until he was discharged as a technical sergeant in June, 1946.

In September, 1946, he entered the Graduate College of the University of Illinois and obtained a Master of Science degree in chemistry in 1947. From 1946 to 1949 he held a teaching assistantship in the Division of Analytical Chemistry.

The author is a member of the American Chemical Society and Sigma Xi.

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